Local density of states subject to finite impurity concentration in graphene

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It is demonstrated that there is a characteristic impurity concentration, at which variation with concentration and overall appearance of the local density of states at the impurity site in graphene are changing their behavior. Features that are prominent in the local density of states for the single impurity are disappearing from it when impurity concentration far exceeds this critical value. The impurity subsystem not only induces the rearrangement of the electron spectrum in graphene, but also undergoes a substantial spectral transformation by itself, which can be observed experimentally.

Introduction. The spectrum rearrangement, which is inherent in disordered systems, have been studied for a large variety of systems over a period of last decades [1, 2, 3]. In essence, this phenomenon is grounded on the indirect interaction of impurities through the host system. The impurity state that is formed close to the band edge, or in the vicinity of any other van Hove singularity, has an effective radius that is large compared to the lattice constant. Thus, the spatial overlap of such impurity states occurs at the low impurity concentration ($c \ll 1$). This overlap results in a radical alteration of spectral properties of the disordered system, which is especially pronounced near the energy of the impurity state.

Predominantly, the spectrum rearrangement is talked about with regard to a remarkable change in the dispersion relation or in the total density of states. However, with recent advances in the scanning tunneling spectroscopy (STS), it became possible to observe directly the local density of states (LDOS) [4, 5, 6]. Thus, it seems reasonable to inquire how the spectrum rearrangement might be reflected in the shape of the LDOS.

Below we would try to examine whether an increase in the impurity concentration influence the behavior of the LDOS to such an extent, so that it is permissible to speak about the impurity induced rearrangement of the LDOS on its own account. It is well known that an increase in the impurity concentration throws a veil over the LDOS features that correspond to a single impurity in the system [7, 8, 9]. In this connection, it should be stressed that we will be well within our rights introducing the concept of the impurity induced rearrangement of the LDOS only in a case, when qualitatively different regimes in the LDOS behavior can be distinguished, and the critical concentration that indicates the transition from one regime to another is closely related to the spatial overlap of the impurity states.

Our treatment of this issue is based on a straightforward model for graphene [10]. Because graphene is a purely two–dimensional (2D) object, the STS measurements of the electronic LDOS in this material are decidedly natural. Moreover, possibilities of the resonance state formation and respective features in the single impurity LDOS at the impurity site and in its neighborhood have been discussed elsewhere [11, 12, 13]. Opportunities to check up by future STS experiments on these characteristics in the near field of the impurity have been already addressed [14], and first reports on the STS measurements in graphene have been published recently [15].

Model. For the sake of simplicity we consider a substitutional binary alloy with a diagonal disorder in the tight–binding approximation. This uncomplicated model of a disordered system is attributed by tradition to Lifshitz [16]. It features absolute randomness in space distribution of impurities. We choose the asymmetric definition of impurity perturbation. Consequently, the on–site potentials are V_L with the probability c, or 0 otherwise. The corresponding Hamiltonian reads,

$$\boldsymbol{H} = \boldsymbol{H}_0 + \boldsymbol{H}_{imp}, \qquad \boldsymbol{H}_{imp} = V_L \sum_{\boldsymbol{n},\alpha}' c_{\boldsymbol{n}\alpha}^\dagger c_{\boldsymbol{n}\alpha}, \qquad (1)$$

where $\boldsymbol{n}$ refers to lattice cells, α enumerates sublattices, $c_{\boldsymbol{n}\alpha}^\dagger$ and $c_{\boldsymbol{n}\alpha}$ are electron creation and annihilation operators. The summation in Eq. (1) is restricted to those sites that are occupied by impurities. Since the impurity perturbation is local in its character, the main physics of graphene in the linear dispersion domain can be captured by a model 2D system with a single Dirac cone in the spectrum. Thus, the host Hamiltonian $\boldsymbol{H}_0$ can be written in the following way,

$$\boldsymbol{H}_0 = \sum_{\boldsymbol{k}}[f(\boldsymbol{k})c_1^\dagger(\boldsymbol{k})c_2(\boldsymbol{k}) + f^*(\boldsymbol{k})c_2^\dagger(\boldsymbol{k})c_1(\boldsymbol{k})], \quad (2)$$

$$c_\alpha(\boldsymbol{k}) = \frac{1}{\sqrt{N}}\sum_{\boldsymbol{n}} e^{i\boldsymbol{k}\boldsymbol{n}} c_{\boldsymbol{n}\alpha}, \quad f(\boldsymbol{k}) = \frac{a}{2\sqrt{\pi}}(k_x + ik_y),$$

where the magnitude of the hopping parameter is chosen so that the bandwidth is unity, when the Brillouin zone is approximated with a circle. Then, the diagonal element of the host Green's function (GF) $\boldsymbol{g} = (\epsilon - \boldsymbol{H}_0)^{-1}$ in the vicinity of the Dirac point is given by [13, 17]

$$g_{\boldsymbol{n}\alpha\boldsymbol{n}\alpha}(\epsilon) \equiv g_0(\epsilon) \approx 2\epsilon \ln|\epsilon| - i\pi|\epsilon|, \quad |\epsilon| \ll 1. \quad (3)$$

Single impurity problem. In a case, when only a single impurity is present in the lattice, the diagonal element of the GF $\mathcal{G} = (\epsilon - \mathbf{H})^{-1}$ at the impurity site becomes

$$\mathcal{G}_0(\epsilon) = g_0(\epsilon)/[1 - V_L g_0(\epsilon)], \qquad (4)$$

For a sufficiently large impurity perturbation V_L, the respective single impurity local density of states (LDOS) $\rho_{imp}(\epsilon) = -\pi^{-1} \operatorname{Im} \mathcal{G}_0(\epsilon)$ manifests a resonance peak [13]. This peak is analogous in its nature to the resonances described in unconventional superconductors [4]. Its energy is provided by the Lifshitz equation,

$$1 = V_L \operatorname{Re} g_0(\epsilon_r) \approx 2 V_L \epsilon_r \ln |\epsilon_r| . \qquad (5)$$

The solution of this equation, i.e., the resonance energy ϵ_r is located above the Dirac point in the spectrum for perturbation $V_L < 0$, and vice versa. This property of the resonance state holds valid for any two symmetric bands touching each other at a certain energy. By grouping Eqs. (3) and (4) together, obtain,

$$\rho_{imp}(\epsilon) = |\epsilon|/[(1 - 2V_L \epsilon \ln |\epsilon|)^2 + (\pi V_L \epsilon)^2]. \qquad (6)$$

Power series expansion of the denominator in Eq. (6) about the resonance energy yields,

$$\rho_{imp}(\epsilon) \approx |\epsilon| \Gamma_r^2 / \{[\pi V_L \epsilon_r]^2 [(\epsilon - \epsilon_r)^2 + \Gamma_r^2]\},$$
$$\Gamma_r = \pi |\epsilon_r| / [2|1 + \ln |\epsilon_r||], \qquad (7)$$

Thus, the LDOS has the Lorentz profile in the vicinity of the resonance, when it is located so close to the Dirac point, that the inequality

$$\gamma_r \equiv \frac{\Gamma_r}{|\epsilon_r|} \approx \frac{\pi}{2\,|1 + \ln |\epsilon_r||} \ll 1 \qquad (8)$$

is fulfilled. As a rule, a resonance is accepted as a well–defined, when this condition is met.

Finite impurity concentration. It is convenient to consider conditional (or weighted) GFs when dealing with the finite impurity concentration. The conditional GF with the first site occupied by an impurity,

$$\mathcal{G}^{(imp,host)} = V_L^{-1} \mathbf{H}_{imp} \mathcal{G}, \qquad (9)$$

can be represented through the self–energy after averaging over possible impurity distributions [18, 19],

$$\mathbf{G}^{(imp,host)} = V_L^{-1} \mathbf{\Sigma} \mathbf{G}, \qquad \mathbf{G} = \mathbf{g} + \mathbf{g} \mathbf{\Sigma} \mathbf{G}, \qquad (10)$$

where $\mathbf{G} = \langle \mathcal{G} \rangle$ is the averaged GF of the system. As long as the impurity concentration remains sufficiently small to neglect multiple occupancy corrections, the self–energy can be approximated by means of the well–known modified propagator method [20],

$$\mathbf{\Sigma} \approx \sigma \mathbf{I}, \qquad \sigma = c V_L/[1 - V_L g_0(\epsilon - \sigma)]. \qquad (11)$$

The self–energy, which is identical on both sublattices owing to the symmetry, is also site–diagonal within this approximation. In order to obtain a quantity that can be related to $\mathcal{G}_0(\epsilon)$ in a single impurity problem, the diagonal in lattice indices element of the conditional GF should be properly scaled with the impurity concentration,

$$c^{-1} G_0^{(imp,host)} \approx g_0(\epsilon - \sigma)/[1 - V_L g_0(\epsilon - \sigma)]. \qquad (12)$$

Thus, we get an expression that formally resembles Eq. (4), in which the host GF $\mathbf{g}$ is replaced by the propagator of the disordered system $\mathbf{G}(\epsilon) \approx \mathbf{g}(\epsilon - \sigma)$. Finally, the average LDOS at the impurity site can be written down through the self–energy,

$$\rho_{loc}(\epsilon) \approx -\frac{1}{\pi} \operatorname{Im}\Big[\frac{g_0(\epsilon - \sigma)}{1 - V_L g_0(\epsilon - \sigma)} + \frac{1}{V_L}\Big] =$$
$$= -\frac{1}{\pi V_L} \operatorname{Im} \frac{1}{1 - V_L g_0(\epsilon - \sigma)} = -\frac{1}{\pi} \frac{\operatorname{Im} \sigma}{c V_L^2}. \qquad (13)$$

With the help of the standard substitution,

$$\epsilon - \sigma = \varkappa \exp(i\varphi), \quad \varkappa > 0, \quad 0 < \varphi < \pi, \qquad (14)$$

the imaginary part of the self–consistency condition in Eq. (11) becomes,

$$c V_L^2 \left[2 \ln \varkappa + (2\varphi - \pi) \cot \varphi\right] +$$
$$+ \left[1 - V_L \varkappa(2 \ln \varkappa \cos \varphi - (2\varphi - \pi) \sin \varphi)\right]^2 +$$
$$+ \left[V_L \varkappa(2 \ln \varkappa \sin \varphi + (2\varphi - \pi) \cos \varphi)\right]^2 = 0, \qquad (15)$$

where the particular form of the host GF (see Eq. (3)) has been taken into account. At the given impurity perturbation V_L and the given impurity concentration c, this equation always has two solutions for the phase φ, when $\varkappa$ exceeds some threshold value. In a turn, both roots provide corresponding magnitudes of the energy, when substituted into the real part of Eq. (11),

$$\epsilon = \varkappa \cos \varphi + c V_L \left[1 - V_L \varkappa(2 \ln \varkappa \cos \varphi - (2\varphi - \pi) \sin \varphi)\right] / \left\{[1 - V_L \varkappa(2 \ln \varkappa \cos \varphi - (2\varphi - \pi) \sin \varphi)]^2 + [V_L \varkappa(2 \ln \varkappa \sin \varphi + (2\varphi - \pi) \cos \varphi)]^2\right\}. \qquad (16)$$

The LDOS from Eq. (13) can be expressed in the same variables too,

$$\rho_{loc}(\epsilon) = \varkappa \sin \varphi/(\pi c V_L^2). \qquad (17)$$

Several examples of the LDOS at the impurity site, which were calculated according to Eqs. (15)-(17), are depicted in Figs. 1–2 for a range of impurity concentrations.

Rearrangement of resonance peak. In a parallel to the single impurity problem, the resonance energy that corresponds to the given impurity concentration should be a solution of the equation (cp. to Eq. (5)),

$$1 = V_L \operatorname{Re} G_0(\epsilon_r(c)). \qquad (18)$$

By using Eq. (3) and the substitution (14), this equation can be recast as follows,

$$1 = 2V_L\epsilon_r(c)[\ln|\epsilon_r(c)/\cos\varphi_r(c)| + \\ + (\pi/2 - \varphi_r(c))\tan\varphi_r(c)]. \quad (19)$$

From here on, we will assume without any loss of generality that $\epsilon_r > 0$ to make expressions more readable. When the concentration is low enough to keep $\varphi_r(c)$ small, an approximate solution of Eq. (19) is:

$$\epsilon_r(c) \approx \epsilon_r[1 + \gamma_r\varphi_r(c)], \qquad \varphi_r(c) \ll 1. \quad (20)$$

Thus, because γ_r (see Eq. (8)) is the resonance width parameter that should be small for the well–defined quasilocalized state, the energy of resonance varies slowly with $\varphi_r(c)$. The concentration dependence of $\varphi_r(c)$ can be obtained from the self–consistency condition (15). The second term in Eq. (15) is zero by the definition of $\epsilon_r(c)$, the remaining two lead to the relation,

$$c = -2\epsilon_r^2(c)\tan\varphi_r(c) \times \quad (21) \\ \times (\ln|\epsilon_r(c)/\cos\varphi_r(c)|\tan\varphi_r(c) + \varphi_r(c) - \pi/2).$$

As above, Eq. (21) considerably simplifies while the phase at the resonance energy $\varphi_r(c)$ remains small,

$$c \approx \pi\epsilon_r^2(c)\varphi_r(c)(1 + \varphi_r(c)/\gamma_r), \qquad \varphi_r(c) \ll 1. \quad (22)$$

This relation reveals a hidden physical meaning of parameter γ_r. It clearly shows that γ_r is the characteristic phase for the resonance state. The corresponding impurity concentration is given by Eq. (22) with $\varphi_r(c) = \gamma_r$,

$$c_r = -\frac{\pi^2\epsilon_r^2(c_r)}{1 + \ln\epsilon_r} \approx -\frac{\pi^2\epsilon_r^2}{1 + \ln\epsilon_r} \approx -\frac{\pi^2\epsilon_r^2}{\ln\epsilon_r}. \quad (23)$$

At the critical impurity concentration c_r the damping of the resonance induced by the disorder becomes equal to the damping of the single impurity state, $-\operatorname{Im}\sigma \approx \epsilon_r(c_r)\varphi_r(c_r) \approx \Gamma_r$, and, respectively, the LDOS at the resonance energy decreases to the one half of its magnitude for the single impurity problem (see Eq. (7)),

$$\rho_{loc}(\epsilon_r(c_r)) \approx \frac{\epsilon_r(c_r)\varphi_r(c_r)}{\pi c_r V_L^2} = \frac{1}{2}\frac{1}{\pi^2 V_L^2\epsilon_r} = \frac{\rho_{imp}(\epsilon_r)}{2}. \quad (24)$$

Neglecting the concentration offset in the resonance position (20), Eq. (22) can be easily solved for the phase,

$$\varphi_r(c) \approx (\gamma_r/2)(\sqrt{1 + (8c/c_r)} - 1), \quad (25)$$

Consequently, the concentration dependence of the resonance peak height in the LDOS at the impurity site immediately follows from Eqs. (24) and (25),

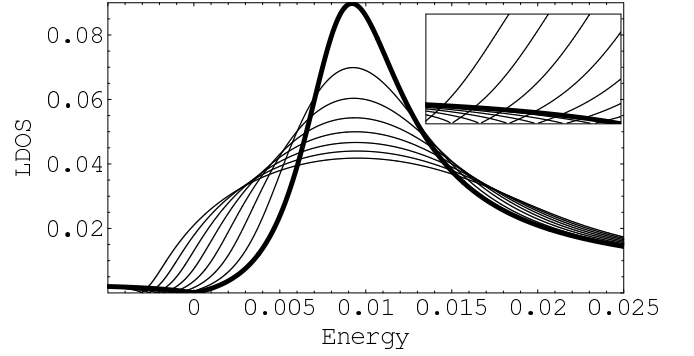$$\rho_{loc}(\epsilon_r(c)) \approx \frac{\sqrt{1 + (8c/c_r)} - 1}{(4c/c_r)}\rho_{imp}(\epsilon_r). \quad (26)$$

FIG. 1: The LDOS at the impurity site for $\epsilon_r = 0.01$ at $c = 4n \times 10^{-5}$, $n = 1, 2\ldots 7$. The single impurity LDOS is displayed for comparison by the thick line. The peak height is decreasing with increasing the concentration. The inset is showing the bottom left hand corner at a larger scale.
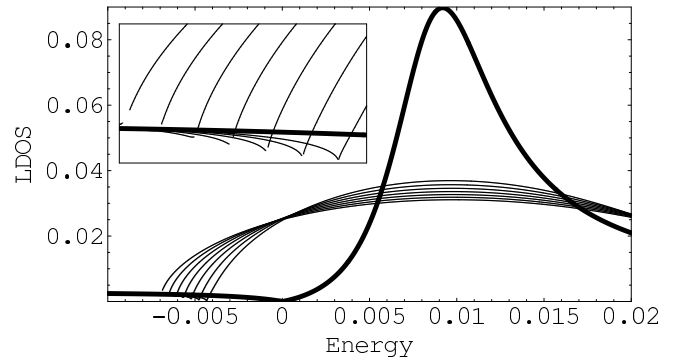

FIG. 2: The LDOS at the impurity site for $\epsilon_r = 0.01$ at $c = (36+4n) \times 10^{-5}$, $n = 1, 2\ldots 7$. The single impurity LDOS is displayed for comparison by the thick line. The peak height is decreasing with increasing the concentration. The inset is showing the bottom left hand corner at a larger scale.

With increasing impurity concentration, this height decreases linearly with concentration at the start,

$$\rho_{loc}(\epsilon_r(c)) \approx [1 - (2c/c_r)]\rho_{imp}(\epsilon_r), \qquad c \ll c_r, \quad (27)$$

but then the rate of this gradual decrease slows down,

$$\rho_{loc}(\epsilon_r(c)) \approx \sqrt{c_r/(2c)}\rho_{imp}(\epsilon_r), \qquad c \gg c_r. \quad (28)$$

The difference between these two regimes is clearly evident from the comparison of Fig. 1 with Fig. 2. In principle, it should be feasible to capture the change of the rate at which the magnitude of the LDOS at the resonance energy varies with the impurity concentration by STS measurements, not to mention the halving of the resonance peak height. Thus, we expect that the task of pinpointing the critical concentration of the spectrum rearrangement, which is a valuable parameter of the system, is accessible by actual experiments.

Rearrangement of antiresonance. Apart from the resonance, there is also a noticeable dip in the LDOS shape

close to the Dirac point in the host system, which can be considered like a kind of an antiresonance. At low impurity concentration the position of this dip practically coincides with those energy in the spectrum, at which $\varphi = \pi/2$. At this energy the imaginary part of the self–consistency condition Eq. (11) reads,

$$- \operatorname{Im} \sigma = \varkappa_{dip} = -\frac{2cV_L^2 \varkappa_{dip} \ln \varkappa_{dip}}{1 + 4V_L^2 \varkappa_{dip}^2 \ln^2 \varkappa_{dip}}, \qquad (29)$$

while the effective shift due to impurities is given by

$$\epsilon_{dip}(c) \equiv \operatorname{Re} \sigma = \frac{cV_L}{1 + 4V_L^2 \varkappa_{dip}^2 \ln^2 \varkappa_{dip}}. \qquad (30)$$

As usual, the characteristic concentration for this point in the spectrum should be determined by the relation $|\operatorname{Re}\sigma| = |\operatorname{Im}\sigma|$. This condition yields,

$$c_{dip} = -4\epsilon_r^2 \ln |\epsilon_r|. \qquad (31)$$

For $c \ll c_{dip}$, the magnitude of the LDOS at this specific energy is rapidly increasing with impurity concentration,

$$\rho_{loc}(\epsilon_{dip}(c)) \approx (2/\pi)\{\exp[-1/(2cV_L^2)]/(2cV_L^2)\}, \qquad (32)$$

and then is reaching its maximum value at $c = c_{dip}$,

$$\rho_{loc}(\epsilon_{dip}(c_{dip})) = (2\pi|V_L|)^{-1}. \qquad (33)$$

According to Eq. (30), the dip position is gradually displaced approximately by the amount cV_L with increasing the impurity concentration for $c \ll c_{dip}$, and, finally, this dip totally disappears from the LDOS at the impurity cite at $c \sim c_{dip}$. The described detachment of the LDOS curve from the energy axis can be distinctly seen in the inset of the Fig. 2.

Discussion   In a system with the linear dispersion, the GF variation with the intersite distance has the characteristic radius that is proportional to $1/|\epsilon|$. Since in a 2D system the average distance between impurities is proportional to $1/\sqrt{c}$, the anticipated magnitude of the critical concentration of the spectrum rearrangement is sitting around ϵ_r^2. Two critical concentrations (23) and (31) that were argued for above are bracketing from both sides this crude estimation. There is an intimate interdependence of this LDOS rearrangement and the rearrangement of the whole electron spectrum, which have been studied in [13]. It is not difficult to verify that the validity criterion introduced in [13] is completely supporting the results derived here. Within the plain impurity model adopted, the well–defined resonance state is possible only for a strong impurity perturbation. However, the restrictions imposed on the resonance appearance for, say, the double impurity should not be that severe [14, 21, 22], while the main physics of the LDOS rearrangement must remain substantially the same. Analogous effect can be achieved by a tuning of the impurity–host hopping parameter.

Conclusion.   In summary, we have demonstrated that the concept of the LDOS rearrangement is fully justified. The sharper and the closer to the Dirac point is the resonance, the lower is the critical concentration of the LDOS rearrangement. The respective critical concentration should not be exceeded for the resonance peak and the antiresonance dip to be discernible in the shape of the LDOS at the impurity site. We presume that the LDOS rearrangement is not specific to graphene or related systems with the Dirac dispersion, and should occur in virtually any system that manifests impurity states in the close vicinity of the van Hove singularities in its spectrum.

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